

Synthesis, characterization and electrocatalytic activity of silver nanorods towards the reduction of benzyl chloride

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Received 3 October 2007; received in revised form 9 February 2008; accepted 13 February 2008

Available online 17 February 2008

Abstract

This paper describes a simple method of synthesizing silver nanorods using the polyol process, where propylene glycol serves both as a reducing agent and as a solvent in the presence of a capping reagent such as polyvinylpyrrolidone (PVP). The diameter and length of silver nanorods could be controlled by changing the AgNO_3/PVP ratio. The end-to-end assembly of the silver nanorods was found. The silver nanorods were characterized by using scanning electron microscopy, transmission electron microscopy, X-ray diffraction and absorption spectroscopy. The catalytic activity of a glassy carbon electrode with Ag nanorods exhibits extraordinary electrocatalytic activities towards the electro-reduction of benzyl chloride.

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Keywords: Silver nanorods; Polyol process; Reducing agent; Capping reagent; Electro-reduction

1. Introduction

Nanomaterials of noble metals have received much attention due to their potential application in microelectronics, optical and catalytic properties [1–5]. The synthesis of metal nanoparticles of desired size and shape has enormous importance in nanotechnology because of their characteristic shape and size dependent optical, electronic and chemical properties. The novel properties of these materials have found extensive uses in microelectronics, electronics, magnetic devices, non-linear optics, chemical and biochemical sensors and in catalysis [5–7]. Among the known nanoparticles, Ag is widely studied because of its characteristic optical, spectroscopic and catalytic properties. They have been widely exploited for use in photography, catalysis, biological labeling, photonics and surface enhanced Raman scattering, among others. A rich variety of recipes are now available in the literature for the synthesis of Ag nanoparticles. However, it has been observed in most cases, that due to the existence of a highly exposed surface, the nanoparticles tend to aggregate and form large clusters even during the preparative process. Therefore, a need to control the particle–particle interactions

so as to obtain a stable dispersion has been acutely felt by researchers in this community. It is generally accepted that the preparation of discrete silver nanoparticles with well-defined shape and well-controlled dimensions is more difficult than preparation of gold ones due to the higher reactivity of silver compounds. Here we report the formation of silver nanorods, through direct reduction of AgNO_3 by the solvent (propylene glycol) at 170 °C in the presence of a stabilizer polymer PVP. By varying the concentration of silver salt and PVP as well as the temperature, one can conveniently control the shape of the resulting nanoparticles. These results are in agreement with those reported by Xia and co-workers in a number of recent papers using the polyol process [8–12]. It was shown that silver nanorods formed in a modified polyol process as a result of the aggregation of previously formed nanoparticles.

An exciting and hitherto unexploited silver nanorod has been needed for electrode applications. Electrocatalytic reduction of organic halides (RX) has been a central topic in organic electrochemistry for the last few decades [13–17]. Among various examined electrode materials, silver has been found to possess extraordinary electrocatalytic properties [18–32].

In the present paper, we report a simple chemical synthesis of silver nanorods. The as-prepared silver nanorods were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), powder X-ray diffraction (XRD) and UV absorption spectrum measurements. The

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electrochemical reduction of benzyl chloride is evaluated by cyclic voltammetry and is interpreted in comparison with that of conventional silver electrodes. Here we report the results of an investigation on the potentialities of silver nanorods as an electrocatalyst in the electro-reduction of benzyl chloride.

2. Experimental

2.1. Materials

Poly (*N*-vinyl-2-pyrrolidone) (PVP, MW \sim 40 000, supplied by Fluka), silver nitrate (AgNO_3) and the solvents used in the study were analytical grade reagents and were used as received.

2.2. Synthesis of silver nanorods

The synthesis was performed within a three-neck round beaker, which was heated in an oil bath up to 170 °C and then 10 ml of AgNO_3 and 20 ml of PVP solution in glycol were added in turn. The refluxing was maintained for 90 min; small

aliquots were then withdrawn during the reaction for TEM. The mixture was diluted with water and nanorods were collected by centrifugation.

2.3. Structural characterization

XRD patterns were obtained by a powder diffractometer (XRD-SHIMADZU XD-D1) using a Ni-filtered $\text{Cu K}\alpha$ X-ray radiation source. The morphology of the silver nanorods was investigated by SEM (FEI, Model: Quanta 200). TEM, electron diffraction and energy dispersive X-ray analysis (EDAX) were performed on a Philips CM12/STEM instrument. For UV–vis absorption investigation, a certain amount of the obtained Ag nanorod powders was dispersed in ethanol and determined with a TU-1201 model spectrophotometer.

2.4. Electrochemical characterization

A single glass compartment cell with three electrodes was employed for the cyclic voltammetry studies. Pt wire and

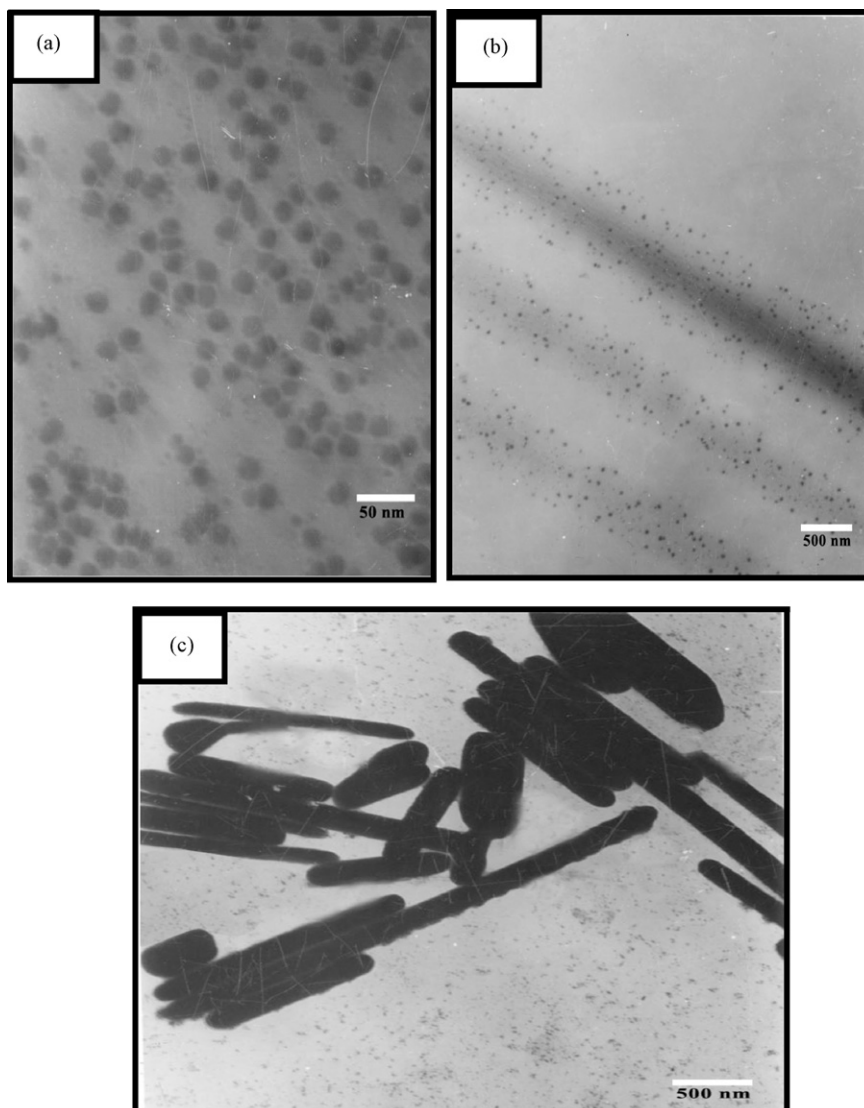


Fig. 1. (a–c) TEM images of silver nanorods formation during the course of reaction.

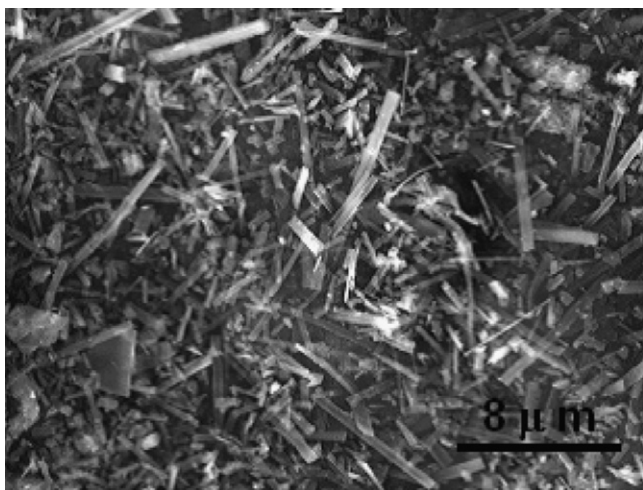


Fig. 2. Scanning electron microscope picture of silver nanorods.

saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. A 0.076-cm^2 area of glassy carbon (GC) or silver served as the working electrode. All electrochemical measurements were performed using a

CHI660A potentiostat/galvanostat. The glassy carbon was first polished with alumina paste (procured from BAS, USA) followed by ultrasonication in water for 5 min; it was then polished with diamond paste ($3\ \mu\text{m}$) and again ultrasonicated for 10 min in water. The nanorods were coated on a glassy carbon electrode using nafion as the binder and dried in an oven at $80\ ^\circ\text{C}$ for 2 min to get a thin film on glassy carbon electrode. The electrolyte was degassed with nitrogen gas before the electrochemical measurements.

3. Results and discussion

The formation of nanorods of silver can be visually observed through a continuous color change from pale yellow during the formation of initial seeds in the solution upon addition of AgNO_3 solution through red and green towards gray, as the particles grow. A general observation in our TEM studies was the presence of stripes made of small dots in the early stages of the reaction, in contrast with long continuous rods when the solution was allowed to boil for 90 min. Typical images are shown in Fig. 1. It is clear that initially only small spherical dots of nanoparticles exist (Fig. 1a); as the reaction proceeded

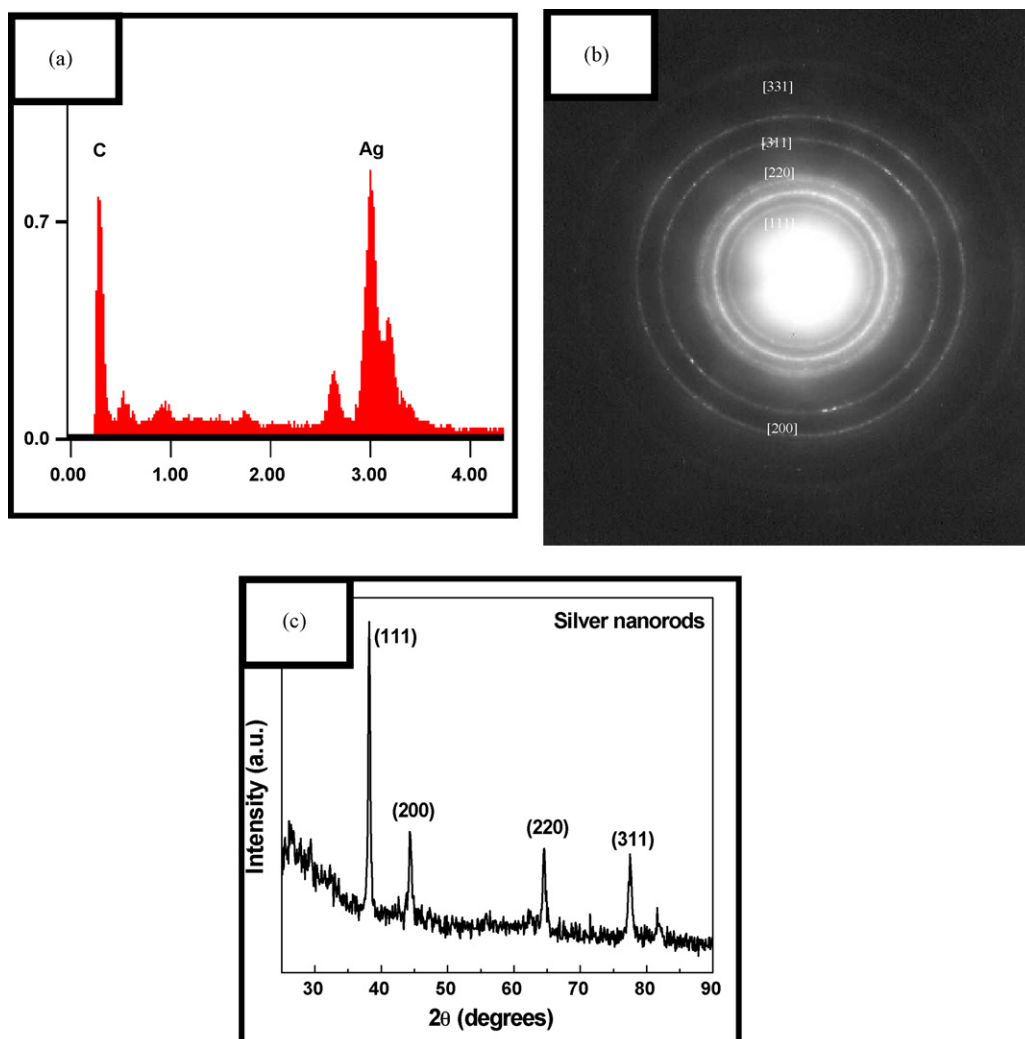


Fig. 3. (a) EDX spectra (b) electron diffraction pattern and (c) XRD pattern of silver nanorods (X-ray source: $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\ \text{\AA}$)).

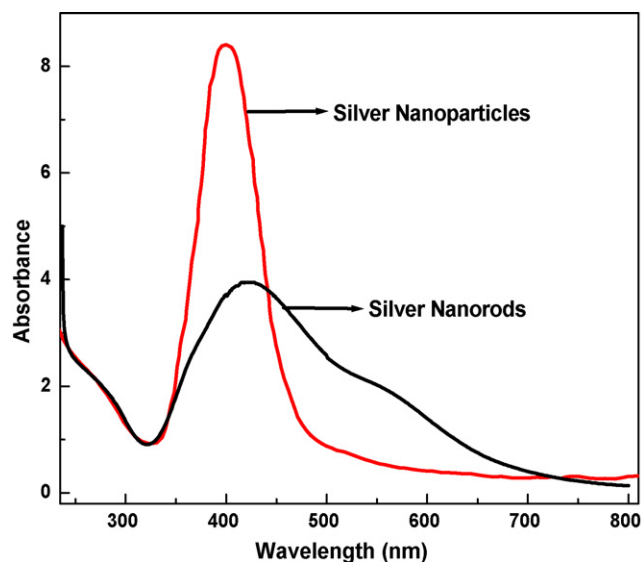


Fig. 4. UV–vis spectra of silver nanoparticles and nanorods.

further stripes (Fig. 1b) of various lengths and thickness for. As the reaction proceeds, well-defined rods are eventually obtained (Fig. 1c). SEM (Fig. 2) results also show the well-defined rods of silver.

The energy-dispersive X-ray analysis (Fig. 3a) of a sample provides further evidence that the product is silver. Fig. 3b displays the electron diffraction pattern formed by directing an electron beam onto the silver nanorods. The pattern shows that the silver nanorod tends to growth as a bicrystalline twinned structure. On the basis of these findings, it is concluded that nanorods consist of crystalline silver.

The structure of as-prepared silver nanorods was investigated by XRD analysis. A typical XRD pattern of the silver nanorods synthesized using the polyol process was found to possess a face centered cubic structure (fcc) as shown in Fig. 3c. Four distinct diffraction peaks were observed at 2θ values of 38.1° , 44.3° , 64.4° and 77.3° , respectively, corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystalline planes of cubic Ag (JCPDS cards 4-0783). The result was similar to that reported [33]. The broad nature of the XRD peaks could be attributed to the nano-size of the particles (Fig. 3c).

It is very interesting to investigate the optical properties of silver since it absorbs strongly in the visible region due to surface plasmon resonance [34,35]. The position of the plasmon absorption peak depends on the particle size and shape [36–38]. The UV–vis spectra of the silver nanoparticles and nanorods are shown in Fig. 4. The silver nanoparticles display plasmon absorption in the visible region and usually have an absorption maximum at 404 nm [38]. The silver nanorods showed two plasmon bands in the UV–vis absorption spectrum one at 424 nm and the other at wavelengths ranging from 500 to 680 nm depending on the length of the nanorods. Silver nanorods display an absorption maximum at 424 nm, which is red-shifted about 20 nm compared to the silver nanoparticles [39]. The bigger the aspect ratio the more red shifted is the longitudinal plasmon band [40].

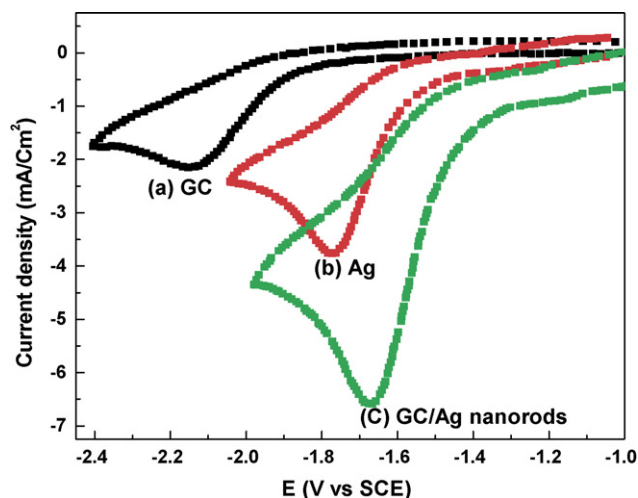


Fig. 5. Cyclic voltammograms recorded at 0.2 V s^{-1} in $\text{CH}_3\text{CN} + 0.1 \text{ M Et}_4\text{NClO}_4$ at (a) GC electrode (b) Ag electrode and (c) GC/Ag nanorod electrodes.

We investigated the electro-reduction of benzyl chloride at silver and GC electrodes. Two types of silver electrode were used: one made from the bulk metal and the other was made from glassy carbon-modified Ag nanorods (denoted GC/Ag nanorods). On all three electrodes, a single irreversible peak is observed in cyclic voltammetry. Fig. 5 shows examples of cyclic voltammograms obtained for the electro-reduction of benzyl chloride at GC, Ag and GC/Ag nanorod electrodes. As shown in Fig. 5, benzyl chloride exhibits a single irreversible reduction peak at all electrodes. The voltammetric behaviour of benzyl chloride at Ag is quite similar to that observed at GC except for the remarkable positive shift of the peak. Such a positive shift is indicative of the catalytic role of Ag in the electrode process [41]. The position of the peak, however, depends strongly on the electrode material. A significant positive shift was observed at the silver nanorod electrodes. The data obtained at GC, Ag and GC/Ag nanorod electrodes are collected in Table 1.

The most important result emerging from such studies is that silver nanorods exhibits extraordinary electrocatalytic activities towards the electro-reduction process, especially in the case of benzyl chloride. There is more positive shift in the reduction potential for glassy carbon modified Ag nanorods electrode compared to that for a polycrystalline Ag electrode. The extraordinary electrocatalytic effect of Ag nanorods is probably related to the diffusion controlled process occurring at the surface of the nanorods and to the high affinity of the Ag nanorods with chloride ions.

Table 1
Voltammetric data for the reduction of benzyl chlorides (3 mM) in $\text{CH}_3\text{CN} + 0.1 \text{ M Et}_4\text{NClO}_4$ at $v = 0.2 \text{ V s}^{-1}$

Electrode	Potential ^a (V)	Current density (mA/cm ²)
GC	-2.14	2.2
Ag	-1.77	3.7
GC/Ag nanorods	-1.66	6.5

^a Applied potential (V vs. SCE).

4. Conclusion

In summary, we have shown that silver nanorods form in glycol solution through aggregation of smaller, spheroidal nanoparticles at high temperature during reduction of AgNO_3 in the presence of PVP, under appropriate experimental conditions. It is found that the concentrations of both AgNO_3 and PVP play an important part in the formation of nanorods. In conclusion, Ag nanorods have shown good catalytic properties in the electro-reduction of benzyl chlorides. Although the catalytic properties of Ag nanorods originate from its affinity for the chloride ions, the possibility of extraordinary electrocatalytic effect of Ag nanorods is linked to the morphology of the nanorods.

References

- [1] R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W.J. Mahoney, R.I. Osifchin, *Science* 273 (1996) 1690.
- [2] A.P. Alivasatos, *Science* 271 (1996) 933.
- [3] M. Moffit, A. Eisenberg, *Chem. Mater.* 7 (1995) 1178.
- [4] M.A. El-Sayed, *Acc. Chem. Res.* 34 (2001) 257.
- [5] M. Valden, X. Lai, D.W. Goodman, *Science* 281 (1998) 1647.
- [6] C.J. Murphy, *Science* 298 (2002) 2139.
- [7] P.V. Kamat, *J. Phys. Chem. B* 106 (2002) 7729.
- [8] N.R. Jana, T.K. Sau, T. Pal, *J. Phys. Chem.* 103 (1999) 115.
- [9] S.K. Ghosh, S. Kundu, M. Madal, T. Pal, *Langmuir* 18 (2002) 8756.
- [10] Y. Sun, B. Gates, B. Mayers, Y. Xia, *Nano Lett.* 2 (2002) 165.
- [11] Y. Sun, Y. Xia, *Adv. Mater.* 14 (2002) 833.
- [12] Y. Sun, Y. Yin, B.T. Mayers, T. Herricks, Y. Xia, *Chem. Mater.* 14 (2002) 4736.
- [13] J.-M. Savéant, *Adv. Phys. Org. Chem.* 26 (1990) 1.
- [14] O.R. Brown, H.R. Thrisk, B. Thornton, *Electrochim. Acta* 16 (1971) 495.
- [15] D.D. Tanner, J.A. Plambeck, D.W. Reed, T.W. Mojelsky, *J. Org. Chem.* 45 (1980) 5177.
- [16] D.A. Koch, B.J. Henne, D.E. Bartak, *J. Electrochem. Soc.* 134 (1987) 3062.
- [17] C.P. Andrieux, A. Le Gorande, J.-M. Savéant, *J. Am. Chem. Soc.* 114 (1992) 6892.
- [18] S. Rondinini, P.R. Mussini, V. Ferzetti, D. Monti, *Electrochim. Acta* 36 (1991) 1095.
- [19] S. Rondinini, P.R. Mussini, P. Muttini, G. Sello, *Electrochim. Acta* 46 (2001) 3245.
- [20] M. Benedetto, G. Miglierini, P.R. Mussini, F. Pelizzoni, S. Rondinini, G. Sello, *Carbohydr. Lett.* 1 (1995) 321.
- [21] S. Rondinini, P.R. Mussini, G. Sello, E. Vismara, *J. Electrochem. Soc.* 145 (1998) 1108.
- [22] M. Guerrini, P. Mussini, S. Rondinini, G. Torri, E. Vismara, *Chem. Commun.* (1998) 1617.
- [23] S. Rondinini, P.R. Mussini, G. Cantu, G. Sello, *Phys. Chem. Chem. Phys.* 1 (1999) 2989.
- [24] M. Fedurco, C.J. Sartoretti, J. Augustynski, *Langmuir* 17 (2001) 2380.
- [25] S. Ardizzone, G. Cappelletti, P.R. Mussini, S. Rondinini, L.M. Doubova, *J. Electroanal. Chem.* 532 (2002) 285.
- [26] A.A. Isse, A. Gennaro, *Chem. Commun.* (2002) 2798.
- [27] S. Ardizzone, G. Cappelletti, L.M. Doubova, P.R. Mussini, S.M. Passeri, S. Rondinini, *Electrochim. Acta* 48 (2003) 3789.
- [28] P.R. Mussini, S. Ardizzone, G. Cappelletti, L.M. Doubova, M. Longhi, S. Rondinini, *J. Electroanal. Chem.* 552 (2003) 213.
- [29] A. Gennaro, C.M. Sánchez-Sánchez, A.A. Isse, V. Montiel, *Electrochem. Commun.* 6 (2004) 627.
- [30] A.A. Isse, M.G. Ferlin, A. Gennaro, *J. Electroanal. Chem.* 581 (2005) 38.
- [31] C. Bellomunno, D. Bonanomi, L. Falciola, M. Longhi, P.R. Mussini, L.M. Doubova, G. Di Silvestro, *Electrochim. Acta* 50 (2005) 2331.
- [32] A.A. Isse, L. Falciola, P.R. Mussini, A. Gennaro, *Chem. Commun.* (2006) 344.
- [33] J.J. Zhu, S.W. Liu, O. Palchik, Y. Kolytyn, A. Gedanken, *Langmuir* 16 (2000) 6369.
- [34] S. Kapoor, *Langmuir* 14 (1998) 1021.
- [35] P. Mulvaney, S. Underwood, *Langmuir* 10 (1994) 3427.
- [36] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, *J. Phys. Chem. B* 107 (2003) 668.
- [37] K.S. Lee, M.A. El-Sayed, *J. Phys. Chem. B* 110 (2006) 19220.
- [38] T. Itakura, K. Torigoe, K. Esumi, *Langmuir* 11 (1995) 4129.
- [39] S. Link, M.B. Mohamed, M.A. El-Sayed, *J. Phys. Chem. B* 103 (1999) 3073.
- [40] N.R. Jana, L. Gearheart, C.J. Murphy, *J. Phys. Chem. B* 105 (2001) 4065.
- [41] A.A. Isse, A. De Giusti, A. Gennaro, L. Falciola, P.R. Mussini, *Electrochem. Commun.* 8 (2006) 1707.